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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to an electrolysis solution and a rechargeable battery. It is related with the electrolysis solution used for the rechargeable battery and it whose safety under a overcharge situation improved in detail.

[0002]

[Description of the Prior Art]For example, the electrolysis solution which dissolved lithium salt in the solvent which makes a subject nonaqueous solvents, such as carbonic ester, ether, and lactone, as an electrolysis solution for lithium secondary batteries is known. These nonaqueous solvents are solvents outstanding on a battery characteristic, such as excelling also in the stability at the time of cell use highly [a dielectric constant], since oxidation potential is high.

[0003]On the other hand, although use with potential high for the high stability of this nonaqueous solvent is possible for the electrolysis solution using the above nonaqueous solvents therefore, what is called a overcharge phenomenon that becomes the voltage more than predetermined upper limit voltage conversely at the time of charge, etc. poses a problem easily. Since phenomena, such as ignition and a burst, can also be caused not only modification and generation of heat of a cell but when excessive if it becomes a surcharge, it is important to raise the safety of the rechargeable battery at the time of overcharge.

[0004]Especially, as positive active material of a lithium secondary battery, since the capacity per weight is large, lithium transition metal multiple oxides which have the layer structure, such as a lithium cobalt oxide (LiCoO_2) and a lithium nickel oxide (LiNiO_2), are mentioned as a leading material, but. Since these compounds will be in the state where the lithium ion almost ****ed in the overcharging condition, it may become unstable, and an electrolysis solution and a rapid exoergic reaction may be caused or a lithium metal may be deposited on a negative electrode, the safety at the time of overcharge is dramatically important.

[0005]As a trial which raises the safety at the time of such overcharge conventionally, a overcharge inhibitor is added in an electrolysis solution and the method of intercepting current is known. Namely, when aromatic compounds, such as biphenyl which has the oxidation potential beyond the upper limit voltage value of a cell, are added in an electrolysis solution as a overcharge inhibitor and it is in an overcharging condition. When the above-mentioned aromatic compounds carry out oxidative polymerization and form the tunic of high resistance in an active material surface, it is how to suppress overcharge current and stop advance of a

surcharge (for example, each gazette of JP,9-106835,A, the patent No. 2939469, and the patent No. 2983205).

[0006]

[Problem(s) to be Solved by the Invention]However, the actual condition was being unable to say that the above-mentioned overcharge prevention method is also enough. For example, the biphenyl and 3-chlorothiophene which are the overcharge inhibitors indicated to JP,9-106835,A, Fracs may have an adverse effect on a battery characteristic, and since the terphenyl derivative which is the overcharge inhibitor indicated in the patent No. 2939469 gazette has the low solubility to an electrolysis solution, the fall of battery capacity may be brought about, The diphenyl ether which is the overcharge inhibitor indicated in the patent No. 2983205 gazette had the problem of it having been strong and being hard to treat a pungent smell.

[0007]Then, the new overcharge inhibitor which has sufficient overcharge preventive effect was called for. [0008]

[Means for Solving the Problem]This invention is made in view of the above-mentioned problem, and the purpose aims at prevention of a surcharge more outstanding using an effective overcharge inhibitor, and there is in improving safety at the time of overcharge. As a result of repeating examination wholeheartedly that this invention persons should attain the above-mentioned purpose, as a overcharge inhibitor, Dicarboxylic acid diester which is not a conventionally publicly known aromatic system compound, and its derivative, If a overcharge inhibitor of a publicly known aromatic-compounds system is conventionally used together, a preventive effect of a more outstanding surcharge will be demonstrated, And by using together comparatively little above-mentioned dicarboxylic acid diester and a derivative of those, and a overcharge inhibitor of a conventionally publicly known aromatic-compounds system to a solvent which makes a subject nonaqueous solvents, such as carbonic ester, ether, and lactone, It found out that safety at the time of sufficient overcharge was securable, and this invention was completed based on this knowledge.

[0009]Namely, in an electrolysis solution which dissolves lithium salt in a solvent in which a gist of this invention makes a subject at least one sort of nonaqueous solvents chosen from a group which consists of carbonic ester, ether, and lactone, It consists without an electrolysis solution, wherein the above-mentioned solvent contains dicarboxylic acid diester (however, except for succinic acid diester) and its derivative, and with a molecular weight of 500 or less aromatic compounds.

[0010]Other gists of this invention consist without a rechargeable battery having the above-mentioned electrolysis solution, an anode, and a negative electrode.

[0011]

[Embodiment of the Invention]Hereafter, it explains to details per embodiment of the invention. The solvent used for the electrolysis solution of this invention makes a subject at least one sort of nonaqueous solvents chosen from the group which consists of carbonic ester, ether, and lactone. Content of these nonaqueous solvents is of 50 % of the weight or more usually preferably made into 100 % of the weight still more preferably 80% of the weight or more to the whole solvent. When there are too few rates that the above-mentioned nonaqueous solvent occupies, the problem that degradation accompanying the fall of the electrical conductivity of an electrolysis solution, etc. and the oxidation-reduction reaction of an electrolysis solution is large may arise.

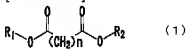
[0012]As carbonic ester which can be used as the above-mentioned nonaqueous solvent, Chain carbonic

ester, such as cyclic carbonate, such as propylene carbonate (PC) and ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), can be illustrated. Dimethoxyethane (DME), diethoxyethane (DEE), etc. can be illustrated as ether which can be used as the above-mentioned nonaqueous solvent.

[0013]Gamma-butyrolactone (GBL), gamma-valerolactone, etc. can be illustrated as lactone which can be used as the above-mentioned nonaqueous solvent. Although at least one sort of carbonic ester, ether, and lactone should just be used for the above-mentioned nonaqueous solvent, it makes carbonic ester contain preferably. Of course, two or more of these sorts can also be used together. Especially a desirable thing is a mixed solvent with the lactone which are high dielectric constant solvents, such as cyclic carbonate, such as PC and EC, or GBL, and chain carbonic ester which is low viscosity solvents, such as DMC, DEC, and EMC.

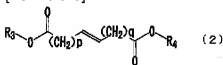
[0014]Dicarboxylic acid diester (however, except for succinic acid diester) and its derivative, and with a molecular weight of 500 or less aromatic compounds are made to contain [in / both / this invention] as a overcharge inhibitor in an electrolysis solution. Dicarboxylic acid dialkyl ester is preferably used as this dicarboxylic acid diester. As a compound suitable as the above-mentioned dicarboxylic acid diester, it is a following general formula (1). : [0015]

[Formula 5]



[0016](R_1 and R_2 express the alkyl group or halogenation alkyl group of the carbon numbers 1-10 among a formula, and n is an integer of 0-1, and 3-10.) -- the saturation dicarboxylic acid diester expressed and following general formula (2): [0017]

[Formula 6]



[0018](R_3 and R_4 express the alkyl group or halogenation alkyl group of the carbon numbers 1-10 among a formula, and p and q are the integers of 0-5, respectively, and are $0 < p+q < 10$.) -- unsaturated-dicarboxylic-acid diester ** expressed is mentioned. R_1 in the above-mentioned general formula (1) and (2) - R_4 are a with an or more 1 carbon number [or less 10] alkyl group or a halogenation alkyl group.

Specifically A methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, An isobutyl group, s-butyl group, t-butyl group, a pentyl group, an isopentyl group, A neopentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group, A decyl group, a fluoromethyl group, difluoromethyl group, a trifluoromethyl group, A trifluoroethyl group, a pentafluoro propyl group, a trifluoroethyl group, A heptafluoro butyl group, a nonafluoro pentyl group, a tetrafluoro propyl group, A hexafluoro butyl group, an octafluoropentyl group, a propylfluoromethyl group, Propyl difluoromethyl group, a propyl trifluoromethyl group, a butylfluoromethyl group, butyl difluoromethyl group, a butyl trifluoromethyl group, a pentafluorobutyl group, a heptafluoro pentyl group, etc. can be mentioned. n in the above-mentioned general formula (1) is

an integer of 0-1, and 3-10, and p and q in a general formula (2) are an integer of 0-5, respectively, and satisfy the expression of relations of $0 \leq p+q \leq 10$. Since it is in the tendency for the solubility over said solvent to fall when the carbon number of the above-mentioned $R_1 - R_4$, n, and p+q exceed ten, there is a possibility that a overcharge preventive effect may fall.

[0019] If it is a compound with a molecular skeleton of dicarboxylic acid diester as the above-mentioned dicarboxylic acid diester, except for succinic acid diester, it will not be limited in particular. These derivatives can also be used. As a derivative, various kinds of compounds which have the above-mentioned dicarboxylic acid diester skeleton, such as what replaced some hydrogen atoms of the above-mentioned dicarboxylic acid diester in a substituent, can be mentioned. As the above-mentioned substituent, for example A halogen atom, an oxygen atom, a sulfur atom, An amino group, an alkylamino group, an arylamino group, a carvone amino group, A sulfonamide group, an oxy-carbonyl-amino group, a oxy sulfonylamino group, An ureido group, hydroxyl, a sulphydryl group, a methoxyl group, a low-grade alkyl group of the carbon numbers 1-3, A cycloalkyl group, an alkoxy group, an alkenyl group, an alkynyl group, an aralkyl group, An aryl group, a cyano group, a nitro group, a formyl group, an aryloxy group, An alkylthio group, an acrylic group, an arylthio group, an acyloxy group, a sulfonyloxy group, An acyl group, an oxycarbonyl group, a carbamoyl group, a sulfonyl group, a sulfinyl group, a oxy sulfinyl group, a sulfamoyl group, a carboxylic acid group or its salt, a sulfonic group or its salt, a phosphonic acid group or its salt, heterocyclic residue, or a hydroxyl group can be mentioned. A carbon number of the above-mentioned substituent is usually five or less preferably ten or less.

[0020] As an example of dicarboxylic acid diester to be used and its derivative, A dimethyl oxalate, a diethyl oxalate, oxalic acid dipropyl, a dibutyl oxalate, An oxalic acid screw (fluoromethyl), an oxalic acid screw (difluoromethyl), Oxalic acid diester, such as an oxalic acid screw (trifluoromethyl), dimethyl malonate, Diethyl malonate, malonic acid dipropyl, dibutyl malonate, a malonic acid screw (fluoromethyl), Malonic diester, such as a malonic acid screw (difluoromethyl) and a malonic acid screw (trifluoromethyl), Dimethyl maleate, a diethyl maleate, maleic acid dipropyl, Dibutyl maleate, a maleic acid screw (fluoromethyl), a maleic acid screw (difluoromethyl), Diester maleate, such as a maleic acid screw (trifluoromethyl), Dimethyl fumarate, diethyl fumarate, fumaric acid dipropyl, fumaric acid dibutyl, Fumarate diester, such as a fumaric acid screw (fluoromethyl), a fumaric acid screw (difluoromethyl), and a fumaric acid screw (trifluoromethyl), glutaric acid dimethyl, glutaric acid diethyl, glutaric acid dipropyl, glutaric acid dibutyl, a glutaric acid screw (fluoromethyl), Glutaric acid diester, such as a glutaric acid screw (difluoromethyl) and a glutaric acid screw (trifluoromethyl), Dimethyl adipate, diethyl adipate, adipic acid dipropyl, Dibutyl adipate, bis adipate (fluoromethyl), bis adipate (difluoromethyl), Di-ester adipate, such as bis adipate (trifluoromethyl), Pimelic acid dimethyl, pimelic acid diethyl, a pimelic acid screw (fluoromethyl), Pimelic acid diester, such as a pimelic acid screw (difluoromethyl) and a pimelic acid screw (trifluoromethyl), Suberic acid dimethyl, suberic acid diethyl, suberic acid dipropyl, Suberic acid dibutyl, a suberic acid screw (fluoromethyl), a suberic acid screw (difluoromethyl), Suberic acid diester, such as a suberic acid screw (trifluoromethyl), Azelaic acid dimethyl, azelaic acid diethyl, azelaic acid dipropyl, Azelaic acid diester, such as azelaic acid dibutyl, an azelaic acid screw (fluoromethyl), an azelaic acid screw (difluoromethyl), and an azelaic acid screw (trifluoromethyl), dimethyl sebacate, diethyl sebacate, sebacic acid dipropyl, Dibutyl sebacate, a sebacic acid screw (fluoromethyl), a sebacic acid screw (difluoromethyl), Sebacic acid diester, such as a sebacic acid screw (trifluoromethyl), Dimethyl undecanedioate, diethyl undecanedioate, dipropyl undecanedioate,

Dibutyl undecanedioate, screw undecanedioate (fluoromethyl), Undecanedioic acid diester, such as screw undecanedioate (difluoromethyl) and screw undecanedioate (trifluoromethyl), Dimethyl dodecanedioate, diethyl dodecanedioate, dipropyl dodecanedioate, Although dodecanedioic acid diester, such as dibutyl dodecanedioate, screw dodecanedioate (fluoromethyl), screw dodecanedioate (difluoromethyl), and screw dodecanedioate (trifluoromethyl), acetone-dicarboxylic acid diethyl, etc. can be mentioned, it is not limited to these. A dimethyl oxalate, a diethyl oxalate, oxalic acid dipropyl especially, A dibutyl oxalate, an oxalic acid screw (fluoromethyl), an oxalic acid screw (difluoromethyl), Oxalic acid diester, such as an oxalic acid screw (trifluoromethyl), dimethyl malonate, Diethyl malonate, malonic acid dipropyl, dibutyl malonate, a malonic acid screw (fluoromethyl), Malonic diester, such as a malonic acid screw (difluoromethyl) and a malonic acid screw (trifluoromethyl), Dimethyl maleate, a diethyl maleate, maleic acid dipropyl, Dibutyl maleate, a maleic acid screw (fluoromethyl), a maleic acid screw (difluoromethyl), Diester maleate, such as a maleic acid screw (trifluoromethyl), Dimethyl fumarate, diethyl fumarate, fumaric acid dipropyl, fumaric acid dibutyl, A fumaric acid screw (fluoromethyl), a fumaric acid screw (difluoromethyl), Fumarate diester, such as a fumaric acid screw (trifluoromethyl), glutaric acid dimethyl, glutaric acid diethyl, glutaric acid dipropyl, glutaric acid dibutyl, a glutaric acid screw (fluoromethyl), a glutaric acid screw (difluoromethyl), Glutaric acid diester, such as a glutaric acid screw (trifluoromethyl), is preferred, Still more preferably Dimethyl malonate, diethyl malonate, malonic acid dipropyl, Dibutyl malonate, a malonic acid screw (fluoromethyl), a malonic acid screw (difluoromethyl), Malonic diester, such as a malonic acid screw (trifluoromethyl), dimethyl maleate, A diethyl maleate, maleic acid dipropyl, dibutyl maleate, A maleic acid screw (fluoromethyl), a maleic acid screw (difluoromethyl), Diester maleate, such as a maleic acid screw (trifluoromethyl), Dimethyl fumarate, diethyl fumarate, fumaric acid dipropyl, fumaric acid dibutyl, A fumaric acid screw (fluoromethyl), a fumaric acid screw (difluoromethyl), It is fumarate diester, such as a fumaric acid screw (trifluoromethyl), It is malonic diester, such as dimethyl malonate, diethyl malonate, malonic acid dipropyl, dibutyl malonate, a malonic acid screw (fluoromethyl), a malonic acid screw (difluoromethyl), and a malonic acid screw (trifluoromethyl), most preferably. Of course, a derivative of these concrete compounds can be used preferably similarly.

[0021]As for dicarboxylic acid diester to be used and its derivative, what is dissolved in the above-mentioned nonaqueous solvent is preferred. When solubility is too low, a problem that an effective addition for acting as a overcharge inhibitor is not obtained may arise. Not less than 100 ** of the boiling point is usually not less than 120 ** preferably. When the boiling point is too low, it volatilizes inside a cell, and bulging may arise at the time of cell use, or a problem of not acting effectively as an additive agent may arise.

[0022]Of course, dicarboxylic acid diester to be used and its derivative can use two or more sorts together. Although content of dicarboxylic acid diester or its derivative considers it as 5 or less % of the weight to said solvent, it may be 2 or less % of the weight still more preferably 3 or less % of the weight preferably. When there is too much content, a problem of having an adverse effect on a battery characteristic may arise. however -- since it may not act effectively as a overcharge inhibitor if there is too little content -- usually -- it is preferably made still more preferably more than 0.5% weight 0.25% of the weight or more 0.1% of the weight or more.

[0023]Although these compounds are not clear about a reason for having a overcharge preventive effect by a little addition, Li metal and dicarboxylic acid diester which were probably generated to a negative electrode at the time of overcharge reacted within a cell, and have guessed that they will stop advance of a surcharge. Now, a more outstanding overcharge preventive effect is demonstrated by using together the above-

mentioned dicarboxylic acid diester and with a molecular weight of 500 or less which oxidizes conventionally in publicly known overcharge potential regions aromatic compounds in this invention. When these aromatic compounds are independently added to an electrolysis solution, the deposit Li of the shape of a dendrite produced with a negative electrode at the time of overcharge and a polymerization film produced on an anode may short-circuit, and it may lead to big generation of heat inside a cell. This generation of heat becomes a trigger of a run away reaction of a cell, and is dangerous. On the other hand, when dicarboxylic acid diester is used together like this invention. As a result of controlling a deposit of the shape of a dendrite Li on a negative electrode at the time of overcharge or a very big resistance component's arising at a reaction with an oxidation product of said aromatic compounds, it is guessed that it becomes difficult to produce a short circuit, therefore a safer overcharge preventive effect is demonstrated.

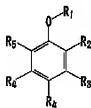
[0024]As a compound suitable as aromatic compounds which oxidize in the above-mentioned conventionally publicly known overcharge potential regions, it is a following general formula (3). : [0025]

[Formula 7]



[0026](among a formula, the phenyl group which may have a hydrogen atom, a halogen atom, a chain alkyl group of the carbon numbers 1-10, an annular alkyl group of the carbon numbers 4-10, or a substituent may be expressed, it may join mutually together, and R₁ - R₆ may form the ring.) -- the compound expressed and following general formula (4): [0027]

[Formula 8]



[0028](R₁ among a formula the phenyl group which may have a chain alkyl group of the carbon numbers 1-10, an annular alkyl group of the carbon numbers 4-10, or a substituent) [express and] R₂ - R₆ express the phenyl group which may have a hydrogen atom, a halogen atom, a chain alkyl group of the carbon numbers 1-10, an annular alkyl group of the carbon numbers 4-10, or a substituent. It may join mutually together and R₁ - R₆ may form the ring. The compound expressed is mentioned.

[0029]What has the oxidation potential in a range which are 4.3-4.9V in these aromatic compounds is preferred. Oxidation potential can be measured by the following cyclic voltammetry method here.

[Measuring method of oxidation potential] Only a bottom section exposed platinum of 1.6 mmphi Working pole, H type cell which made a lithium metal a counter electrode and a reference pole and into which the working pole and counter electrode side was divided with a glass filter is used, What carried out 0.15 mmol/g addition of the aromatic compounds used as a sample is put into an electrolysis solution which dissolved

LiPF_6 in a mixed solvent of the volume ratio 7:3 of EC and DEC by concentration of 1 mol/L at this cell.

Subsequently, potential of a working pole is swept with a sweep rate of 20mV/second to the oxidation side (to the ** side). Potential into which current density of 0.5 mA/cm² flows at this time is specified as oxidation onset potential. Measurement is performed at a room temperature (near 25 **) for convenience.

[0030]Oxidation potential of aromatic compounds of below 4.9V measured by the above method is less than 4.7V preferably. When oxidation potential is too high, it is in a tendency for an overcharge preventive effect to become small. However, since a battery characteristic may usually be degraded in response to the time of cell use of conditions when oxidation potential is too low, more than 4.4V makes [more than 4.3V] oxidation potential more than 4.5V still more preferably preferably.

[0031]As a suitable compound which suits the above-mentioned conditions, biphenyl and its derivative, cyclohexylbenzene and its derivative, a dibenzofuran and its derivative, terphenyl and its derivative, diphenyl ether, its derivative, etc. can be mentioned, for example. The amount of the with an above-mentioned molecular weight of 500 or less aromatic compounds used is usually 0.1 to 10 % of the weight to a solvent.

[0032]If vinylene carbonate or vinyl ethylene carbonate is used together in addition to the above-mentioned dicarboxylic acid diester, its derivative, and with a molecular weight of 500 or less aromatic compounds, Since it not only demonstrates a further outstanding overcharge preventive effect, but becomes possible to also raise the other characteristics, such as the preservation stability of a cell, and a cycle characteristic, it is desirable. The amount of vinylene carbonate and the vinyl ethylene carbonate used is usually 0.1 to 10 % of the weight to a solvent.

[0033]An electrolysis solution of this invention contains lithium salt in a solvent. As lithium salt, LiClO_4 , LiAsF_6 , LiPF_6 , LiBF_4 , $\text{LiB}(\text{C}_6\text{H}_5)_4$, LiCl , LiBr , LiCH_3SO_3 , LiCF_3SO_3 , $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$, $\text{Li}(\text{SO}_2\text{CF}_3)_3$, $\text{LiN}(\text{SO}_3\text{CF}_3)_2$, etc. can be mentioned. Of course, two or more sorts may be mixed and these may be used. Also in the above, it is preferred to use LiBF_4 and LiPF_6 , 0.5-1.5 mol /of concentration of lithium salt is [l.] usually 0.75-1.25 mol/l. preferably to the whole electrolysis solution. Even if lithium salt concentration is too high and it is too low, a fall of electric conductivity may occur, and a battery characteristic may have an adverse effect.

[0034]The electrolysis solution can contain an ingredient of further others if needed. As other ingredients, various kinds of additive agents and surface-active agents for forming a tunic (SEI) in an active material surface of a cell can be mentioned, for example. An electrolysis solution of this invention can be used for rechargeable batteries, such as a lithium secondary battery. A rechargeable battery of this invention is constituted including an anode, a negative electrode, and said electrolysis solution. Although used as an ingredient of an electrolyte layer between an anode and a negative electrode, as long as said electrolysis solution can raise safety at the time of overcharge, it may usually be used anywhere in a cell.

[0035]As an active material of an anode which constitutes a rechargeable battery of this invention, a lithium transition metal multiple oxide is used preferably. As a lithium transition metal multiple oxide, LiCoO_2 .

Although lithium manganese multiple oxides, such as lithium nickel complex oxide, such as lithium cobalt multiple oxides, such as LiNiO_2 , and LiMn_2O_4 , etc. can be mentioned, This invention is effective when using a lithium transition metal multiple oxide of a large cobalt system of lithium content, and a nickel series, i.e., a lithium

cobalt multiple oxide, and lithium nickel complex oxide as an active material of an anode especially. These lithium transition metal multiple oxide can also be stabilized by replacing some transition metal elements which serve as a subject with other metal kinds, such as aluminum, Ti, V, Cr, Mn, Fe, Co, Li, nickel, Cu, Zn, Mg, Ga, and Zr, and is preferred. Of course, two or more sorts of active materials of an anode can also be used together.

[0036]As an active material of a negative electrode which constitutes a rechargeable battery of this invention, although occlusion and a substance which may be emitted can be used for lithium, carbonaceous material is preferred. As an example of this carbonaceous material, a pyrolysis thing of an organic matter in various pyrolysis conditions, an artificial graphite, natural graphite, etc. are mentioned, for example. An artificial graphite and a graphitization mesophase microsphere which were manufactured by high temperature heat treatment of easy graphite pitch suitably obtained from various raw materials, Material which performed various surface treatments which contain a pitch in other artificial graphites, such as graphitization mesophase pitch system carbon fiber, and refining natural graphite, or these black lead is used. Such carbonaceous material has that preferred whose d value (interlaminar distance) of a lattice plane (002nd page) for which it asked by an X diffraction by Gakushin method is 0.335-0.34 nm, and what is 0.335-0.337 nm is more preferred. As for ash, it is preferred that it is 1 or less % of the weight, it is more preferred that it is 0.5 or less % of the weight, and it is preferred that it is especially 0.1 or less % of the weight. It is preferred that crystallite size (L_c) for which it asked by an X diffraction by Gakushin method is not less than 30 nm, it is more preferred that it is not less than 50 nm, and it is preferred that it is especially not less than 100 nm. It can mix to such carbonaceous material further, and other active materials which can emit [occlusion and] lithium can also be used for it. As an active material which can emit [occlusion and] lithium other than carbonaceous material, metallic-oxide materials, such as tin oxide and oxidized silicon, and also a lithium metal, and various lithium alloys can be illustrated. Two or more kinds may be mixed and these negative pole materials may be used.

[0037]The above-mentioned anode and a negative electrode usually contain the above-mentioned active material and a binder, respectively. As a binder, polyvinylidene fluoride, polytetrafluoroethylene, styrene-butadiene rubber, polyisoprene rubber, butadiene rubber, etc. can be mentioned. Conducting materials, such as carbon materials, such as metallic materials, such as copper and nickel, graphite, and carbon black, can also be made to contain in an electrode if needed furthermore. About especially an anode, it is preferred to make a conducting material contain.

[0038]It is not limited in particular for a method of manufacturing an electrode. For example, add a binder, a thickener, a conducting material, a solvent, etc. to an active material if needed, and it is considered as slurry form. It can apply to a substrate of a charge collector and can manufacture by drying, and roll forming of this active material can be carried out as it is, and it can be considered as a sheet electrode or can also be considered as a pellet electrode with compression molding. As a thickener, carboxymethyl cellulose, methyl cellulose, hydroxymethylcellulose, ethyl cellulose, polyvinyl alcohol, oxidation starch, phosphorylation starch, casein, etc. are mentioned.

[0039]as the charge collector which can be used for an electrode -- as a negative pole collector -- metal, such as copper, nickel, and stainless steel, or an alloy -- copper being mentioned preferably and as a positive pole collector, metal, such as aluminum, titanium, and tantalum, or an alloy -- aluminum and its alloy can be mentioned preferably. In a rechargeable battery, a separator is usually infixed between an anode and

a negative electrode. Although not limited in particular for construction material or shape of a separator to be used, it is stable to an electrolysis solution and it is preferred as a liquid-retentive outstanding material to use a porous sheet or a nonwoven fabric etc. which uses polyolefines, such as polyethylene and polypropylene, as a raw material.

[0040] Especially about a method of manufacturing a nonaqueous secondary battery concerning this invention which has a negative electrode, an anode, and a nonaqueous electrolyte at least, it is not limited but can choose suitably from methods usually adopted. A cylinder type which was not limited in particular for shape of a cell, but made a sheet electrode and a separator spiral shape, It is usable in a coin type etc. which laminated a cylinder type, a pellet electrode, and a separator of an inside-out configuration which combined a pellet electrode and a separator.

[0041]

[Example] Hereafter, although an example explains the concrete mode of this invention in detail, this invention is not limited by the following examples unless the gist is exceeded.

[Production of an anode] An anode 90 % of the weight of cobalt acid lithium (LiCoO_2) as positive active material, 5 % of the weight of acetylene black as a conducting agent and 5 % of the weight of polyvinylidene fluorides (PVdF) as a binder are mixed in N-methyl-pyrrolidone solvent, After slurring, it applied to one side of 20-micrometer aluminum foil, and dried, and what was further rolled with the pressing machine was pierced and produced to punching punch 12 mm in diameter.

[Production of a negative electrode] A negative electrode mixes 95 % of the weight of black lead (0.336 nm of spacings) as negative electrode active material, and 5 % of the weight of polyvinylidene fluorides (PVdF) of a binder in N-methyl-pyrrolidone solvent, After slurring, it applied to one side of copper foil of 20-micrometer thickness, and dried, and what was further rolled with the pressing machine was pierced and produced at 12 mm in diameter.

[Assembly of a cell] In the dry box of argon atmosphere, CR2032 type coin cell was used and the lithium secondary battery was produced. Namely, place an anode on a positive electrode can and a 25-micrometer porous polyethylene film is placed as a separator on it, After having added the electrolysis solution after having placed the negative electrode after pressing down with the gasket made from polypropylene, and placing the spacer for thickness adjustment, and making it sink in enough in a cell, the negative electrode can was carried and the cell was obturated. It was considered as the design from which the capacity of a cell becomes the charge maximum 4.2V by the example and a comparative example, and is set to about 4.0 mAh(s) at the discharge minimum 3.0V.

[0042] Under the present circumstances, the ratio of weight [of positive active material] W (c), and weight [of negative electrode active material] W (a), In the anticipated-use upper limit voltage of a rechargeable battery, since the range which does not cause a deposit of a lithium metal on the negative electrode in which the lithium ion emitted from an anode counters was preferred, the capacity factor Rq of a negative electrode and an anode determined the weight so that it might be set to $1.1 \leq Rq \leq 1.2$. the capacity factor Rq -- Q(a) W[x] a) / { Q(c) x W (c) } -- it came out and asked. Electric capacity per weight of the negative electrode active material which can carry out occlusion of the lithium to the maximum was made into Q(a) mAh/g, without Q (c) mAh/g and a lithium metal depositing the electric capacity per weight of positive active material under the conditions corresponding to the initial charging conditions of a cell here. The anode or the negative electrode was used for the working pole, they used the lithium metal for the counter electrode, and Q (c) and Q (a)

constructed and measured the test cell via the separator in the same electrolysis solution as the time of assembling the above-mentioned cell. That is, it asked as the capacity which an anode can charge (discharge of the lithium ion from an anode), and capacity which a negative electrode can discharge (occlusion of the lithium ion to a negative electrode) with the lowest possible current density to the maximum potential of the anode corresponding to the initial charging conditions of the target fuel cell subsystem, or the minimum potential of a negative electrode.

[0043][evaluation of a cell] -- evaluation of a cell -- the initial charge and discharge (capacity check) of (1) -- subsequently -- (2) full charge operations -- it carried out in order of (3) overcharge examinations further. In initial charge and discharge (capacity check), it charged with the constant current constant voltage anodizing process of 1C (4.0 mA) and 4.2V maximum. The cut of charge was considered as the time of a current value reaching 0.05 mA. Constant current performed discharge to 3.0V by 0.2C.

[0044]Full charge operation was charged with the constant current constant voltage anodizing process (0.05-mA cut) of 4.2V maximum. The overcharge examination was considered as 4.99 V cuts or 3hr cut (it cuts in the direction which reached the either point) by 1C. As an index which looks at the superiority or inferiority of a overcharge preventive effect, the coin cell after overcharge was disassembled and the bottom used the value for Li which remains in an anode as overcharge depth in fixed quantity by ultimate analysis. When the anode presentation after a overcharge examination is expressed as Li_xCoO_2 , a surcharge will not progress but a overcharge preventive effect will be so high that x (anode Li ullage) is large.

[0045]Here, it asked for x (anode Li ullage) from the number ratio of mols of Co in the anode for which it asked by ultimate analysis (ICP AEM), and net Li. analysis with the same number of mols of net Li -- Lynn in an anode -- also performing a fixed quantity of (P) and depending this on LiPF_6 -- the total in an anode -- it deducted and asked for Li mol number equivalent to LiPF_6 from Li mol number.

As example 1 electrolysis solution, to the mixed solvent of the volume ratio 3:7 of ethylene carbonate (EC) and diethyl carbonate (DEC). What added 2% of the weight of dimethyl malonate and 2% of the weight of a dibenzofuran was used for the electrolysis solution in which lithium hexafluorophosphate (LiPF_6) was dissolved by the concentration of 1 mol/l. as an additive agent.

[0046]Evaluation of the lithium secondary battery manufactured by said method and Li analysis in the electrode which disassembles the cell after overcharge were conducted. A result is shown in table-1. Evaluation of a lithium secondary battery and Li analysis in the electrode which disassembles the cell after overcharge were similarly conducted except having added further 2% of the weight of the dimethyl malonate and 2% of the weight of vinylene carbonate other than 2% of the weight of a dibenzofuran which were added in example 2 Example 1. A result is shown in table-1.

Evaluation of a lithium secondary battery and Li analysis in the electrode which disassembles the cell after overcharge were similarly conducted except having added 2% of the weight of the diethyl oxalate instead of 2% of the weight of the dimethyl malonate added in example 3 Example 1. A result is shown in table-1.

Evaluation of a lithium secondary battery and Li analysis in the electrode which disassembles the cell after overcharge were similarly conducted except not having added an additive agent in comparative example 1 Example 1. A result is shown in table-1.

Evaluation of a lithium secondary battery and Li analysis in the electrode which disassembles the cell after overcharge were similarly conducted except having added only 2% of the weight of dimethyl malonate as an

additive agent in comparative example 2 Example 1. A result is shown in table-1.

Evaluation of a lithium secondary battery and Li analysis in the electrode which disassembles the cell after overcharge were similarly conducted except having added 2% of the weight of the dibenzofuran instead of 2% of the weight of dimethyl malonate as an additive agent in the comparative example 3 comparative example 2. A result is shown in table-1. The voltage oscillation considered to be based on a short circuit at the time of overcharge was observed, and the apparent overcharge current amount became large.

Evaluation of a lithium secondary battery and Li analysis in the electrode which disassembles the cell after overcharge were similarly conducted except having added 2% of the weight of vinylene carbonate instead of 2% of the weight of dimethyl malonate as an additive agent in the comparative example 4 comparative example 2. A result is shown in table-1.

Evaluation of a lithium secondary battery and Li analysis in the electrode which disassembles the cell after overcharge were similarly conducted except having added 2% of the weight of a dibenzofuran, and 2% of the weight of vinylene carbonate instead of 2% of the weight of dimethyl malonate as an additive agent in the comparative example 5 comparative example 2. A result is shown in table-1. The voltage oscillation considered to be based on a short circuit at the same time of overcharge as the comparative example 3 was observed, and the apparent overcharge current amount became large.

[0047]

[Table 1]

表-1

	添加剤 1	添加剤 2	添加剤 3	過充電試験 過充電電流 量(見掛け)	過充電深度 X in Li ₂ CO ₃	備考
実施例 1	マロン酸 ジメチル	ジベンゾ フラン	なし	49.4mAh/g	0.419	
実施例 2	マロン酸 ジメチル	ジベンゾ フラン	ビニレンカ ーボネート	52.5mAh/g	0.401	
実施例 3	シュウ酸 ジエチル	ジベンゾ フラン	なし	28.3mAh/g	0.501	
比較例 1	なし	なし	なし	81.2mAh/g	0.163	
比較例 2	マロン酸 ジメチル	なし	なし	99.8mAh/g	0.505	
比較例 3	なし	ジベンゾ フラン	なし	327.8mAh/g	0.231	短絡 あり
比較例 4	なし	なし	ビニレンカ ーボネート	86.9mAh/g	0.138	
比較例 5	なし	ジベンゾ フラン	ビニレンカ ーボネート	133.5mAh/g	0.307	短絡 あり

[0048]From table-1, by adding both dicarboxylic acid diester (however, except for succinic acid diester) and its derivative, and with a molecular weight of 500 or less aromatic compounds shows that the safety at the time of overcharge improves. The big difference was not looked at by battery characteristics, such as a capacity maintenance rate after initial service capacity and 5 cycles, with the lithium secondary battery created in the example, and the lithium secondary battery created by the comparative example.

[0049]

[Effect of the Invention]According to this invention, the electrolysis solution which can raise various kinds of battery characteristics, such as a cycle characteristic, a rate characteristic, and capacity, can be provided. The electrolysis solution which can raise the safety at the time of overcharge by a new overcharge inhibitor especially can be provided.

[0050]According to this invention, the cell which improved various kinds of battery characteristics, such as a cycle characteristic, a rate characteristic, and capacity, can be provided. The cell which raised the safety at the time of overcharge by the new overcharge inhibitor especially can be provided.

[Translation done.]